

# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Dyes of the perylene tetracarboxylic acid bis-benzimidazole series.

We BRITISH NYLON SPINNERS LIMITED, of Pontypool, Monmouthshire, Great Britain, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to pigment dyestuffs for textile fibres, yarns and other articles, particularly to pigment dyestuffs for textile fibres and yarns spun from fully synthetic polymeric materials such as polyamides, polyesters, polyolefins and polymers based on polyacrylonitrile.

Dyeing of hydrophobic synthetic fibres, filaments or yarns, hereinafter referred to as filaments, has received a considerable amount of attention particularly during recent years as is evident from the patent literature.

Apart from the difficulties encountered in the discovery of dyestuffs which are both wash and light fast when applied to the filaments or fabric, there is an added problem of obtaining a uniform level of dyeing throughout any package of filaments or over any piece of fabric made therefrom. This latter problem has been particularly associated with filaments spun from synthetic polymers such as polyamides, polyesters and polyolefins in which the yarn is obtained by melt spinning the high molecular weight polymer and is then subjected to a subsequent drawing or stretching process. The lack of uniformity in dyeing is frequently revealed in the form of stripiness in

the made-up fabric owing to filament defects.

To obtain more uniform dyeing and improved wash and light fastness of synthetic filaments it has been proposed to use a mass dyeing technique in which a pigment dyestuff is added to the polymer before spinning. This technique is equally applicable to the incorporation of pigment dyestuffs in filaments obtained either by solution spinning or by melt spinning. The pigment dyestuff may conveniently be incorporated in the synthetic polymer by admixing with the polymer forming ingredients, e.g. with hexamethylene diammonium adipate in the manufacture of polyhexamethylene adipamide, prior to the polymerisation thereof, or it may be added to the polymer chip by any known method prior to melt spinning, or again it may be dispersed in the polymer solution prior to solution spinning.

The pigment dyestuffs employed in the mass coloration of polymers which are to be melt spun are mainly inorganic since organic pigment dyestuffs are frequently not sufficiently thermally stable for this purpose. However some classes of organic pigment dyestuffs are stable at melt spinning temperatures, derivatives of perylene tetracarboxylic acid being a particular example of such a class.

In the specification of British Letters Patent No. 859,288 there has been described, inter alia, the use of perylene 3:4:9:10-tetracarboxy bis-benzimidazole and its derivatives, wherein each benzimidazole group is substituted by alkyl, halogen or alkoxy

groups in the 4 position, as pigment dyestuffs to impart a reddish-blue to reddish-violet shade to articles formed from polyvinyl chloride. Polyamide filaments also exhibit similar shades of dyeing when melt spun in the presence of one of these compounds.

There is, however, a demand for a pigment dyestuff which will impart a true blue, and particularly a navy blue, colour to synthetic filaments such as polyamides.

We have now found that dyestuffs particularly suitable for the mass coloration of synthetic filaments, such as polyamides, are obtained from a novel series of perylene-3:4:9:10 - tetracarboxy-bis-benzimidazole derivatives wherein the aromatic ring of each benzimidazole group bears two alkyl substituents.

Accordingly therefore this invention provides pigment dyestuffs being perylene-3:4:9:10 - tetracarboxy-bis-benzimidazole derivatives bearing in the aromatic ring of each benzimidazole group two alkyl substituents.

Derivatives in which the alkyl substituents are the same and are methyl, viz:—

Perylene - 3:4:9:10 - tetracarboxy - bis (4':5'-dimethyl-benzimidazole)

Perylene - 3:4:9:10 - tetracarboxy - bis (4':6'-dimethyl-benzimidazole)

Perylene - 3:4:9:10 - tetracarboxy - bis (4':7'-dimethyl-benzimidazole)

Perylene - 3:4:9:10 - tetracarboxy - bis (5':6'-dimethyl-benzimidazole)

Perylene - 3:4:9:10 - tetracarboxy - bis (5':7'-dimethyl-benzimidazole),

the benzimidazole groups being numbered in the normal manner, see for example Chemical Abstracts, Fifth Decennial Index, Vols. 41-50 (1947-1956) p. 1628s, have been found to be most useful for the mass coloration of synthetic filaments, the bis(4':6'-dimethyl-benzimidazole) and bis(5':6'-dimethyl-benzimidazole) derivatives in particular imparting a desirable blue colour to polyamide filaments.

This invention also includes within its scope processes for the manufacture of the hereinbefore defined pigment dyestuffs, the mass coloration of filaments and other shaped articles formed from synthetic polymers, e.g. polyamides, using the said pigment dyestuffs and synthetic filaments and other articles containing the said pigment dyestuffs. The pigment dyestuffs may be added to the synthetic polymeric material prior to the melt spinning, solution spinning or moulding thereof, or it may be incorporated in, e.g. a polyamide, by admixing with the polymer forming ingredients prior to the polymerisation thereof.

These perylene derivatives may be prepared by heating perylene-3:4:9:10-tetracarboxylic acid or dianhydride with the

corresponding diamine at elevated temperatures, e.g. from 200 to 250°C., in solvents such as nitrobenzene, trichlorobenzene or quinoline, in the presence of dehydrating agents or hydrochloric acid. The reaction proceeds in two stages; in the first stage only one of the two amine groups reacts to yield a di-imine; the second stage of the reaction taking place upon prolonged heating of the di-imine when the imidazole rings are closed.

Mixtures of our novel pigment dyestuffs, especially those obtained by condensing perylene-3:4:9:10-tetracarboxylic acid or anhydride with 3:4- or 3:5- dimethyl-o-phenylene-diamine are extremely valuable for the coloration of synthetic filaments.

The following examples in which the parts are parts by weight, illustrate the invention but do not limit it:—

#### EXAMPLE 1

Perylene-3:4:9:10-tetracarboxylic dianhydride (10 parts) is added to the stirred solution of 4:5-dimethyl-ortho-phenylene diamine (24.5 parts) in quinoline (100 parts by volume) containing concentrated hydrochloric acid (5 parts by volume) and rinsed in with quinoline (150 parts by volume). The mixture is stirred and heated for 18 hours at 210 to 215°C., the water formed being continuously removed. The cooled suspension is filtered and the solid residue washed with methanol, and then extracted successively with dilute (7%) hydrochloric acid, water, dilute (3%) sodium hydroxide solution and finally washed with water and dried. The dyestuff, perylene-3:4:9:10-tetracarboxy-bis (5':6'-dimethyl-benzimidazole) (15 parts 98% yield) is obtained as a dark blue powder which does not melt below 400°C. The blue powder (1.2 parts) is ground to pass through a 120 mesh sieve and intimately mixed with 66 nylon salt (60 parts), i.e. hexamethylenediammonium adipate, acetic acid (0.65 parts by volume: 1.752 normal) is added and the mixture heated in a nitrogen-purged sealed Carius tube for 3 hours at 220°C. At the end of this time the half-made polymer is broken up and heated in an open tube under a nitrogen atmosphere at 280°C. for 1½ hours. The yarn spun from this polymer by conventional melt spinning techniques and subsequently cold drawn, exhibits a desirable navy blue colour which has good fastness to light and washing and is resistant to chlorite and peracetic bleaches.

#### EXAMPLE 2

Perylene-3:4:9:10-tetracarboxylic dianhydride is reacted with 3:5-dimethyl-ortho-phenylene diamine as described in Example 1 to give a quantitative yield of

perylene-3:4:9:10-tetracarboxy bis-(4':6'-dimethylbenzimidazole) in the form of a blue powder. The dyestuff is incorporated in polyhexamethylene adipamide polymer as in the manner of Example 1. The yarn spun from this polymer by conventional melt spinning techniques and subsequently cold drawn exhibits a desirable blue colour which has good light and wash fastness and is resistant to chlorite and peracetic bleaches.

#### WHAT WE CLAIM IS:

1. Pigment dyestuffs being perylene-3:4:9:10-tetracarboxy - bis - benzimidazole derivatives bearing in the aromatic ring of each benzimidazole group two alkyl substituents.
2. Pigment dyestuffs according to claim 1 wherein the alkyl substituents are the same and are methyl groups.
3. Perylene-3:4:9:10-tetracarboxy - bis (5':6'-dimethyl-benzimidazole).
4. Perylene-3:4:9:10-tetracarboxy - bis (4':6'-dimethyl-benzimidazole).
5. A process for the manufacture of pigment dyestuffs being perylene-3:4:9:10-tetracarboxy-bis-benzimidazole derivatives wherein one equivalent of perylene-3:4:9:10-tetracarboxylic acid or dianhydride is reacted with two equivalents of a dialkyl-1:2-diamino-benzene at an elevated temperature in the presence of an inert diluent and a dehydrating agent or hydrochloric acid.
6. A process according to Claim 5

wherein the dialkyl 1:2-diaminobenzene is 1:2-diamino-3:5-dimethyl benzene or 1:2-diamino-4:5-dimethyl benzene.

7. A process for the mass coloration of filaments and other shaped articles formed by melt spinning, solution spinning or moulding synthetic polymeric materials wherein a pigment dyestuff as claimed in any one of the Claims 1-4 is added to the said synthetic polymeric material prior to the melt spinning, solution spinning or moulding thereof.

8. A process according to Claim 7 wherein the synthetic polymeric material is a polyamide and the pigment dyestuff is added thereto prior to melt spinning into filaments.

9. A process according to Claim 8 wherein the pigment dyestuff is incorporated in the polyamide by admixing with the polymer forming ingredients prior to the polymerisation thereof.

10. Filaments and other shaped articles of synthetic polymeric material whenever coloured by one of the pigment dyestuffs claimed in any one of the Claims 1 to 4.

11. Polyamide filaments or shaped articles whenever coloured by one of the pigment dyestuffs claimed in any one of the Claims 1 to 4.

12. Coloured polyamide filaments substantially as described herein with reference to Examples 1 and 2.

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